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Physica B 340–342 (2003) 609–612
PHYSICA B
www.elsevier.com/locate/physb

Annealing mechanisms of divacancies in silicon

R. Poirier[a], V. Avalos[b], S. Dannefaer[b,*], F. Schiettekatte[a], S. Roorda[a]

[a] *Groupe de Recherche en Physique et Technologie des Couches Minces, Département de Physique, Université de Montréal, C.P. 6128 Succ. Centre-Ville, Montréal, Que., Canada H3C 3J7*

[b] *Physics Department, University of Winnipeg, 515 Portage Avenue, Winnipeg, Man., Canada R3B 2E9*

Abstract

By combining infrared and positron annihilation spectroscopy new insight has been gained into the mechanism(s) by which divacancies in silicon anneal. Isothermal and isochronal annealings of 8 MeV proton irradiated Si strongly suggest two processes, one due to recombination with interstitials and the other due to vacancy agglomeration. The two processes have nearly the same activation energy.

PACS: 61.72.Cc; 61.72.Ji; 68.80.Jh

Keywords: Silicon; Divacancies; Annealing; Positron annihilation

1. Introduction

The divacancy in silicon (V_2) is a radiation-produced defect that is well characterized by electron paramagnetic resonance (EPR) [1], infrared spectroscopy (FTIR) [2] and by positron annihilation spectroscopy (PAS) [3].

Annealing of V_2 starts at $\sim 125^\circ$C in the cases of neutron and proton irradiation and at $\sim 250^\circ$C in the case of electron irradiation, and based on the latter type of irradiation a migration energy of ~ 1.3 eV was found [1]. The mechanism(s) responsible for annealing are not clear, but it seems a common assumption that V_2 migrates to a sink that is not observable by EPR or by FTIR.

In this work FTIR and PAS have been used to investigate isochronal and isothermal annealing, and it is the results from PAS that provide an insight into the nature of the sinks.

2. Experimental

Undoped float-zone silicon was irradiated with 8 MeV protons to a dose of 4×10^{16} cm^{-2} using a beam current of ~ 750 nA: the 300 μm thick wafer was clamped on a Cu block which was cooled by liquid N_2 during irradiation. After irradiation, the samples were allowed to warm up to 300 K, at which temperature about 1% of the vacancies created during irradiation agglomerate into divacancies.

Infrared absorption was made at room temperature as were most of the positron measurements. The absorption band peaking at 1.8 μm

*Corresponding author. Tel.: +1-204-786-9754; fax: +1-204-783-7981.

E-mail address: steen.dannefaer@uwinnipeg.ca (S. Dannefaer).

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doi:10.1016/j.physb.2003.09.240

was used as a measure for the V_2 concentration after subtraction of the (significant) absorption-edge band.

Positron lifetime spectra each contained 10^7 counts and were analyzed [4] using two lifetime components for the unirradiated samples and three for the irradiated samples. In both cases the number of components was the minimum necessary for statistically acceptable fits, i.e., fits that gave normalized χ^2 values of 1.0 ± 0.1.

3. Results and discussion

Table 1 lists representative data for un-irradiated and irradiated samples. The first of the two lifetimes found in the un-irradiated case (216 ps) arises from 91% of the positrons annihilating in the defect-free crystal, and the second lifetime from positrons trapped by vacancy clusters which contain at least 4 vacancies [6]. Large vacancy clusters are ubiquitous in Si according to PAS, but have to the authors knowledge not been observed by other techniques. For the irradiated cases, the first lifetime (103 ps) is reduced from 216 ps due to the irradiation-induced vacancies giving rise to a lifetime of 290 ps. According to the positron trapping model [5] the first lifetime is given by

$$\tau_1 = (1/\tau_B + 1/\kappa)^{-1}. \quad (1)$$

where τ_B is the bulk lifetime (218 ps [3]). The trapping rate, κ, is given by

$$\kappa = I_2(1/\tau_B - 1/\tau_2)/I_1. \quad (2)$$

Using the data from Table 1 the value of τ_1 in the as-irradiated case is calculated to be 96 ± 5 ps. This agrees with the value of 103 ps in Table 1, so it can be concluded that the simple trapping is applicable. The high intensity (81%) of this component prevents direct observation of the 337 ps component, and the 540 ps have too low an intensity to warrant physical interpretation. The 290 ps lifetime has in several positron works been attributed to divacancies, but in view of recent theoretical calculations [6,7], larger clusters may also contribute as will be discussed later.

Table 1
Lifetime data for an unirradiated and an irradiated sample

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_1 (%)	I_2 (%)	I_3 (%)
Unirr.	216 ± 1	—	337 ± 15	91 ± 1.3	—	9 ± 1
Irr.	103 ± 17	290 ± 3	540 ± 55	16 ± 0.7	81 ± 1	2.7 ± 1.5

Lifetime components (τ's) and their respective intensities (I's) are listed.

FTIR resulting from isochronal annealing of irradiated samples are shown in Fig. 1 by the squares and are reproduced from Ref. [8]. Annealing is noticeable at 125°C for the proton irradiated samples, which is $\sim$125°C lower than observed after electron irradiation [1]. This suggests that the damage created by proton (or neutron irradiation) differs from the damage caused by electron irradiation. Isothermal annealing at 85, 100 and 125°C was investigated using PAS and results are shown in Fig. 2. The parameter κ shown on the ordinate is the positron trapping rate (calculated from Eq. (2)) and its value is proportional to the divacancy concentration. The value of κ before annealing is denoted κ_o; so the ratio κ/κ_o expresses the fraction remaining of vacancy related trapping sites. The positron lifetime was unaffected by annealing and had an average value of 295 ± 2 ps.

The fraction remaining approaches asymptotically values that depend on the annealing temperatures, so the partial removal of divacancies between 85°C and 125°C was analyzed by assuming that the trapping rate has two contributions, one that anneals out at low temperatures, κ', and another that does not, κ''. Thus, the experimentally determined ratio κ/κ_o equals $(\kappa' + \kappa'')/(\kappa'_o + \kappa''_o)$, and with $\kappa'' = \kappa''_o$, values of the pertinent parameter κ'/κ'_o are easily calculated, and results are shown in Fig. 3. From these data the activation energy for vacancy removal was determined to be 1.00 ± 0.1 eV using values of κ'/κ'_o in the range of 0.3 to 0.9. Annealing of vacancies proceeded according to a second order process, as shown in Fig. 4, as deduced from the proportionality between $(\kappa'_o/\kappa' - 1)$ and time of annealing. The attempt frequency deduced from the analysis is between 5×10^{12} and 5×10^{13} s^{-1}, which is in good agreement with the atomic

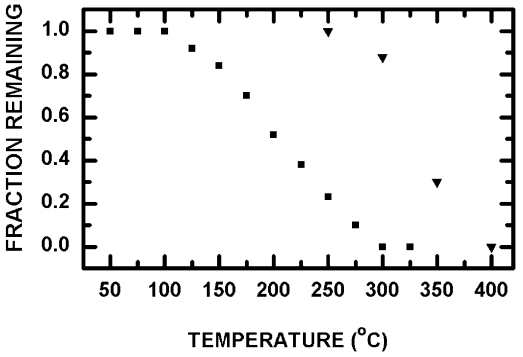

Fig. 1. Fraction remaining of the 1.8 μm absorption band (■) and the V_2^- EPR signal (▼, Ref. [1]) as a function of isochronal (15 m) annealing.

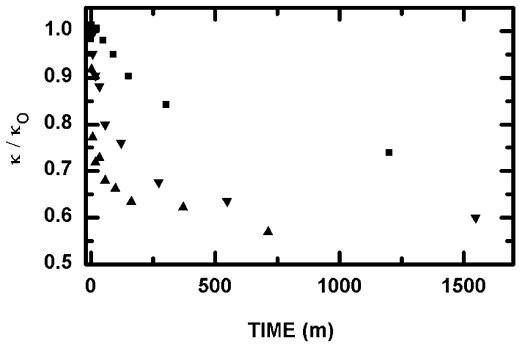

Fig. 2. Fraction remaining of the positron response during isothermal annealing at 85°C (■), 100°C (▼) and 125°C (▲).

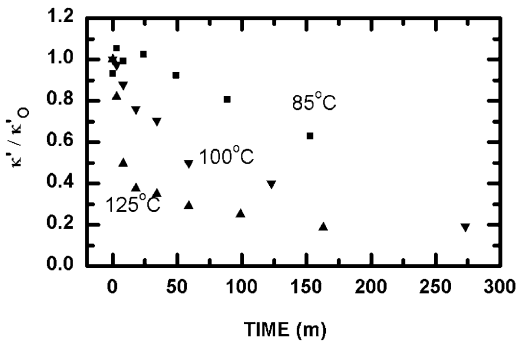

Fig. 3. Fraction remaining after subtraction of the asymptotic values indicated in Fig. 2: 85°C (■), 100°C (▼) and 125°C (▲). The cross-cut method gave an activation energy of 1.00±0.1 eV.

vibrational frequency in silicon. Hence, no significant entropy term needs to be invoked in the migration process.

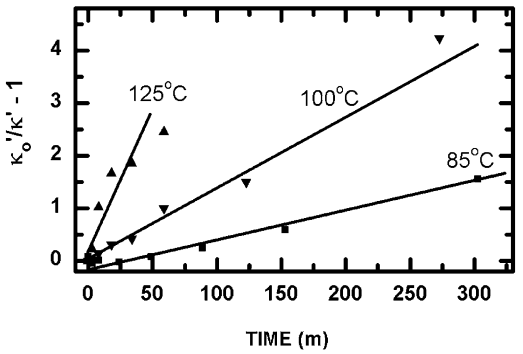

Fig. 4. Plot of $(\kappa'_o/\kappa' - 1)$ versus time which should give a linear relationship in the case of a second-order process.

In view of the agreement between PAS and IR data during low temperature annealing [9] and that the activation energy of 1.0 eV is close to that for diinterstitials [10], but is too low for vacancy migration (1.3 eV), we conclude that stationary divacancies are removed by mobile interstitials. Differential scanning calorimetry qualitatively supports this conclusion by the significant peak of heat release in, the 80–175°C range [8]. It should be pointed out that after electron irradiation, the low temperature annealing is absent (cf. Fig. 1), and this might be a consequence of "light" particle irradiation which cannot create multiple displacements within a small volume.

It was found earlier [9] that an analysis of isothermal annealing at 275°C and 300°C of the 1.8 μm absorption band gave an activation energy of 1.2±0.2 eV and a 2nd order process; the activation energy agrees with former analyses of electron irradiated silicon but not with the order. PAS, on the other hand, showed that the lifetime of 295 ps persisted to temperatures well beyond 300°C, suggesting persistence of divacancies! We have repeated the PAS measurements by doing isochronal annealing experiments to 500°C, while increasing the accuracy of the measurements by a factor of two. The results are shown in Fig. 5, and we can now observe that the positron lifetime does increase, albeit only slightly, upon annealing to 500°C. Thus, vacancy agglomeration does indeed take place, and the small increase in lifetime supports theoretical calculations [6,7] that the vacancies are strung together like in a chain.

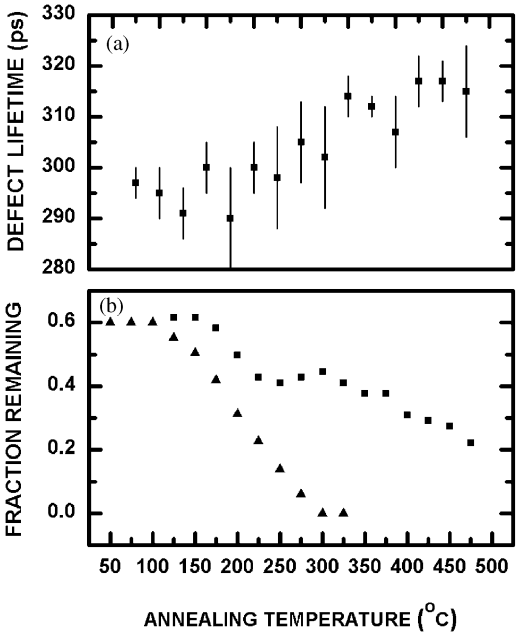

Fig. 5. Isochronal annealing (15 m) of the isothermally annealed sample at 100°C for 1500 m. Positron data are shown together with FTIR data (▲) in panel (b). The fraction remaining is calculated using the amount of response before any annealing.

Annealing above 500°C showed [9] a rapid increase from 300 ps to 420 ps. This indicates that the string-like vacancy agglomerates become unstable and three-dimensional (3-D) vacancy clusters are formed. At the end of annealing the intensity of the 420 ps component was essentially the same as the intensity observed for the grown-in vacancy clusters. These clusters cannot be distinguished from the final trap for the irradiation-produced vacancies.

4. Conclusion

Annealing of divacancies in proton irradiated Si is suggested to consist of two closely overlapping temperature activated processes. The first is due to recombination with interstitials (activation energy 1.0 eV), and the second is due to migration of divacancies, with the well known activation energy of $\sim$1.3 eV.

Data suggest that chains of vacancies are formed during the higher temperature ($\sim$250°C) migration of V_2 and accounts for the disappearance of FTIR absorption at 1.8 μm and the persistence of the vacancy response according to PAS. The chains are stable up to $\sim$500°C, above which they form larger 3-D vacancy clusters.

Acknowledgements

This research was supported by the Natural Science and Engineering Research Council of Canada.

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